

Further Study of Adipic Acid
Degradation in FGD Scrubbers

Radian Corp.
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16. ABSTRACT The report gives results of investigations of adipic acid degradation to account for losses observed during earlier studies where it was used as an additive to improve SO2 scrubber performance. Bench-scale experiments identified the major species resulting from the oxidative degradation of adipic acid, which are: valeric acid, glutaric acid, CO2, CO, carbonate, methane, ethane, propane, and butane. Material balances based on various measurements--including gas chromatography, ion chromatography, and total organic carbon analyses--indicate that all by-products were identified in the laboratory tests: imbalances were less than 10% of the total carbon used. Field tests conducted on a prototype limestone scrubber using adipic acid additive detected only valeric acid and glutaric acid as degradation products. Scrubber sludge was shown to retain 200-500 ppm adipic acid by surface adsorption. In addition, the solids contained 300-800 ppm of occluded adipic acid when precipitated as calcium sulfite; occlusion was only 50 ppm when the solids were oxidized to gypsum.			
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DEGRADATION IN FGD SCRUBBERS

FINAL REPORT

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SECTION 1

INTRODUCTION

This study constitutes a continuation of a recent project performed by Radian Corporation for EPA under Contract #68-02-2608, WA 58 (EPA-600/7-79-224, September 1979). The purpose of the previous program was to determine the mechanisms of the degradation of adipic acid in a limestone-based, SO₂ wet scrubber environment. The addition of adipic acid at a level of 1000-2000 mg/l in the scrubbing solution promotes SO₂ removal and limestone dissolution.

Previous laboratory tests showed that the decomposition of adipic acid could occur through a chemical reaction. No indication of microbial degradation was observed. The chemical process responsible for at least part of the degradation is an oxidative, decarboxylation through a free radical reaction. The initial free radical is produced during the liquid phase oxidation of sulfite to sulfate. The products of this reaction identified to date are valeric acid, butyric acid, glutaric acid, succinic acid, methane, butane, and CO₂. However, the quantities of these products measured in laboratory tests and samples collected from EPA's RTP and Shawnee test facilities did not account for the difference between the quantity of adipic acid added to the systems and that leaving in the waste streams.

The objective of this phase of the study was to provide additional information into the fate of the adipic acid when used in the SO₂ scrubbers. The specific work areas conducted during this present program include:

- more detailed investigation of the degradation products under laboratory simulated scrubber conditions,
- development of improved analytical methods to quantify the organic content of the scrubber solids,
- collection of samples around the oxidation vessel of the venturi/spray tower scrubber at the Shawnee facility for additional characterization of degradation products, and
- identification of the compounds that contribute to the total organic content of the RTP and Shawnee scrubber liquor but were not previously measured by standard organic extraction techniques.

The results of these investigations are presented in the remainder of this report.

SECTION 2

SUMMARY OF RESULTS

The data from the field studies at Shawnee and the bench-scale laboratory tests are summarized in this section. A more detailed presentation of these studies is presented in Sections 4 through 7.

Samples were collected and analyzed from EPA's prototype adipic acid scrubber at the Shawnee facility. Four organic material balances were calculated around the oxidizer tank in the venturi/spray tower scrubber at two different oxidation levels, namely 45 and 95%. Samples collected included inlet and outlet slurry streams and oxidizer vent gases. The following species were detected:

- adipic acid,
- valeric acid,
- glutaric acid,
- succinic acid, and
- carbon monoxide.

The degradation of adipic acid in the oxidation tank was determined by the change in concentration between the oxidizer feed stream and the blowdown stream to thickener. This relation is stated mathematically in the following equation:

$$\text{D.R.} = [\text{Ad}]_i \cdot F_i - [\text{Ad}]_o \cdot F_o \quad (2-1)$$

where

- D.R. = the degradation rate of adipic acid,
[Ad]_i, [Ad]_o = the adipic acid concentrations in the oxidizer inlet and outlet streams, respectively,
F_i, F_o = the flow rates of the oxidizer inlet and outlet streams, respectively,

During the low oxidation conditions approximately 20% of the total adipic acid degradation in the system occurred within the oxidizer. Unexpectedly, the fraction of adipic acid lost across the oxidizer dropped to 10% when the oxidation was increased to 95%. However, the samples were collected during times when the scrubber system was in a mode of transition with respect to both pH and oxidation rate.

Total carbon material balances around the oxidizer closed to within +10%. Valeric acid and glutaric acid were the main degradation products found. Succinic acid and carbon monoxide were minor contributors to the material balance. No light hydrocarbons were detected.

Samples of the scrubber solids were collected to determine whether adipic acid or any degradation products were being coprecipitated or adsorbed with these solids. In the previous adipic acid study the techniques used to characterize the solids were not sensitive enough to detect concentrations below 1000 ppm. Even though concentrations of adipic acid in the solids much below 1000 ppm would not account for all of the losses, a method was developed to lower the detection limits to 10 ppm.

Most of the solid samples were washed after collection and the wash solutions were not retained. Therefore, except for one sample of the forced oxidized solids, only the coprecipitated fraction could be determined. However solids collected from the laboratory studies were treated such that both retention mechanisms could be evaluated. The results of these measurements were:

- scrubber solids consisting of more than 50% $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ contained 300-800 ppm adipic acid in the coprecipitated form,
- scrubber solids consisting of greater than 95% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ contained less than 50 ppm adipic acid in the coprecipitated form,
- one filter cake sample consisting of greater than 95% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was analyzed and found to have 215 ppm adipic acid adsorbed on the surface, and
- fully oxidized solids from the laboratory studies were found to have 300-500 ppm adsorbed adipic acid and less than 50 ppm coprecipitated.

Collection and analysis of samples from the TCA (including sulfite determination) were also accomplished during this program. Results are reported in Section 4.

Total organic carbon (TOC) analysis of Shawnee filtrates showed 20 to 60% more organic carbon than is accounted for by IC or GC methods. The TOC analysis of the extracted filtrates shows the presence of additional organic carbon. No significant amount of material was extractable at neutral or alkaline pH's. Preliminary evidence suggests that the presently unidentified materials are extractable at pH <0.1. This organic species was not observed in the solids produced in the laboratory studies.

In the series of laboratory degradation studies, 60 to 99% of the adipic acid lost from solution was accounted for. Byproducts detected in the material balance tests included the following:

- valeric acid,
- glutaric acid,
- carbon dioxide,
- carbon monoxide,
- carbonate,
- methane,
- ethane,
- propane, and
- butane.

Fluctuations in the liquid phase adipic acid concentration observed in a number of the laboratory tests could not be adequately explained by degradation. Some type of sorption-desorption process between the adipic acid and calcium sulfite seems to be one possible explanation of this variation. The formation of unstable sulfonated organics is another possibility.

Comparisons of gas chromatography (GC), ion chromatography (IC) and total organic carbon (TOC) analyses of samples from the laboratory tests showed moderate agreement between these methods. The data tend to indicate that all by-products were identified in the bench scale tests. Imbalances in the material balances were less than 10% of the original amount of organic material used in the test. Comparison of the bench test results to data obtained from field tests at Shawnee indicate that differences exist which tend to affect the distribution of by-products.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are based on Radian's material balance tests around the bleed-stream oxidizer tank of the venturi/spray tower scrubber at the Shawnee facility:

- the majority of the adipic acid loss did not take place in the oxidizer. Material balances performed under two different operating conditions indicate that 10% to 20% of the total degradation occurred in the oxidizer.
- low molecular weight hydrocarbons were not detected in the Shawnee oxidizer vent.
- carbon monoxide, although identified, was not a significant degradation product in the Shawnee oxidizer.
- glutaric acid and valeric acid were the major degradation products identified.
- presumably CO_2 is a degradation product under field conditions, however, the release of CO_2 during the dissolution of the limestone masks the contribution from degradation.

Analytical methods for determination of organic acids in scrubber solids were improved during this program. Analysis of samples using the new methodology showed that:

- the organic content of the scrubber solids varies as a function of the sulfite to sulfate ratio.
- the concentration of organics adsorbed on the highly oxidized sludges, based upon one sample analysis, was 200-250 ppm. Similar measurements on laboratory generated solids gave results of 300-500 ppm (no coprecipitated adipic acid was measured in either case).
- the contribution of organics associated with the oxidized solids account for approximately 10% of the adipic acid losses from the scrubber.

Various measurements were performed to determine whether all degradation products are being accounted for. In addition to material balance calculations, the TOC data from various fractions were assessed, and compared to data from GC, IC and gravimetric analyses. Based upon these comparisons the following observations were made:

- all major species have been accounted for in bench-scale adipic acid degradation tests.
- based upon the TOC analysis substantial portion, in some cases as much as 50%, of the organic material in Shawnee aqueous samples was unidentified. This material may have been a degradation product or an organic sorbed from the flue gas from the coal-fired boiler. These organics could not be extracted at neutral, alkaline or mild acidic pH's.

The data collected during the course of this program indicate that the primary thrust of future studies should be directed in the following areas:

- identification of the organic material in Shawnee samples which is extracted at $\text{pH} < 0.1$.
- further characterization of the conditions which affect the interaction of adipic acid with the solids in both field and laboratory situations,
- resolution of the differences in the relative amounts of various by-products seen under field conditions as compared to laboratory conditions including investigation of heavy metal effects,
- development of a 'steady-state' laboratory reactor system to more closely simulate field conditions and allow for generation of degradation rate data,
- determine the fate of adipic acid and related degradation associated with the solids under various disposal options, and
- study methods to reduce the degradation rate.

SECTION 4

FIELD SAMPLING RESULTS

The analytical results of the samples collected at the Shawnee Test Facility are presented in this section. Samples were collected around the oxidation vessel (D-108) of the venturi/spray tower scrubber during bleed stream forced-oxidation tests. The specific streams sampled were the feed stream to the oxidizer (AP 1816), the thickener feed (AP 1805) and the sparge air vent. These streams were sampled and analyzed for adipic acid and its degradation products in order to measure the extent of degradation within the oxidizer. The adipic acid was being added in the reaction tank to maintain approximately 1500 ppm.

The details of the sampling approach and analytical results of the three streams are discussed in the following subsections. The results of samples collected from selected points around the TCA test scrubber at Shawnee are also given.

4.1 SAMPLING APPROACH

During April 26 and 27, 1979, four sets of samples were collected around the oxidation tank at the venturi/spray tower scrubber during Shawnee Run 913-1A. The operating configuration during this period involved the use of a common reaction tank for the venturi and spray tower effluents. A bleed stream was taken from the reaction tank and delivered to the oxidation tank where an air sparge was used to oxidize the sulfite to sulfate. The effluent from the oxidizer was then fed to a clarifier and filter.

Two sets of samples were collected at each of two oxidation rates. The sulfite oxidation rate during the first day of sampling was unintentionally low, approximately 30-45 percent. On the second day of sampling the oxidation was greater than 95 percent.

The oxidizer vent was sampled to collect volatile and entrained adipic acid and degradation products. The flow rate of the vented gases was determined from the air sparge rate obtained from the TVA operators' log. The gas sampling train consisted of NaOH impingers for absorption of CO₂ and volatile and entrained organic acids. Downstream of the impingers silica gel and activated carbon traps were used to collect the light hydrocarbons such as methane, ethane, propane and butane.

Two Smith Greenburg impingers containing NaOH solutions were connected to a stainless steel probe using tygon tubing. The hydrocarbon traps were connected in series following the second impinger. The impingers and traps were immersed in an ice bath. The gas sample was pulled through the system using a diaphragm pump and the flow rate was monitored using a calibrated rotameter.

Grab samples of the bleed from the scrubber effluent hold tank to the oxidizer and thickener feed slurries were taken while the gas sampling was being conducted. The slurry samples were subsequently filtered and saved for chemical analysis. One fraction of the filtrate was treated with formaldehyde to stabilize the sulfite concentration for analysis by ion chromatography. A second portion of the filtrate and the filtered solids were saved for analysis of adipic acid and degradation species. All samples were cooled to about 4°C and maintained at this temperature until they were analyzed.

4.2 ANALYTICAL RESULTS OF VENTURI/SPRAY TOWER SAMPLES

The two sample sets collected on April 26 were taken during a period of low oxidation, which was only 30-45 percent even though air was being added. The low oxidation was apparently caused by an increase in the slurry pH which had occurred during the night shift. The pH was lowered and by April 27, during the second sampling period, the oxidation was back up to 95 percent. The operating conditions along with the adipic acid and related degradation products concentrations are summarized in Table 4-1.

Adipic acid concentrations in the filtrate samples were determined using ion chromatographic (IC) and extraction/gas chromatographic (GC) techniques. The GC procedure also was used to identify and quantify other carboxylic acids resulting from the adipic acid degradation. The solid samples were dissolved in an acidified aqueous solution and the organic acids were extracted for analysis.

The NaOH solutions used for the vent gas sampling were analyzed for CO₂ and organic acids. The silica gel and activated carbon traps were thermally desorbed and the off-gases were analyzed using GC. These analytical results are also included in Table 4-1.

4.3 ORGANIC CARBON BALANCE ACROSS OXIDIZER

The concentrations of the various organic compounds measured in the inlet and outlet streams around the oxidation tank were used in conjunction with the respective flow rates to determine the net rate of change in each species within the oxidizer. For comparison purposes the rates are reported as equivalent millimoles of carbon per minute (mmole C/min). In this way, material balance calculations for adipic acid and its degradation products can be obtained by simply comparing the sum of the inlet C with sum of the outlet C. The results of the flow calculations are summarized in Tables 4-2 through 4-5.

TABLE 4-1. VENTURI/SPRAY TOWER OXIDIZER CONDITIONS

Date	Time	Run #	Feed ¹ Stream	Flow Rate (L/min.)	Oxidation (%) ²	Weight Solids (%)	Temp (°C)	pH	Phase	Adipic Acid (ppm)	Glutaric Acid (ppm)	Valeric Acid (ppm)	Succinic Acid (ppm)	Carbon Monoxide (ppm)
4/26	1030	1	BO	102		19.7	48	5.8	Filtrate Solids	1480 820	110 220	36 <5	1.9 <4	-
			TF	102		19.7	44	7.1	Filtrate Solids	1420 380	130 100	12 <5	1.1 <4	-
			OV						Gas	ND ²	ND ²	ND ²	ND ²	ND ²
4/26	1130	2	BO	102		19.7	48	5.7	Filtrate Solids	1330 260	90 100	16 <5	1.6 <4	-
			TF	102		19.7	44	7.1	Filtrate Solids	1260 80	110 40	<0.5 <5	<0.4 <4	-
			OV						Gas	ND ²	ND ²	ND ²	ND ²	ND ²
4/26	1500	-	BO		19.1		53	5.5						
			TF		26.8			6.9						
4/26	2300	-	BO		31.3									
			TF		55.0									
4/27	0700	-	BO		35.8		52	5.1						
			TF		95.0			5.5						
4/27	1000	3	BO	61		11.9	51	5.4	Filtrate Solids	1570 150	95 40	11 <5	4.7 <5	-
			TF	61		13.0	61	5.2	Filtrate Solids	1510 27	190 <4	34 <5	25 <5	-
			FC OV						Gas	215 ND ²	-- .01	-- .23	-- ND ²	47
4/27	1100	4	BO	61		11.9	50	5.5	Filtrate Solids	1570 200	110 80	35 <5	7.5 <4	-
			TF	61		13.0	64	5.5	Filtrate Solids	1560 40	150 <4	27 <5	44 <4	-
			OV						Gas	0.02	0.02	0.23	ND ²	31

¹BO = bleed to oxidizer (AP 1816); TF = Thickener Feed (AP 1805); OV = Oxidizer Vent; FC = Filter Cake
²ND = Not Detected
³Determined by on-site personnel

TABLE 4-2. MATERIAL BALANCE AROUND OXIDIZER TANK (D-108) DURING SAMPLING RUN 1
(4/26/79; LOW OXIDATION CONDITIONS)

Process Stream	Sample Phase	By GC Analysis ¹				By CO Monitor ¹		Total Carbon ¹
		By IC ¹	Adipic Acid	Adipic Acid	Glutaric Acid	Valeric Acid	Succinic Acid	
Bleed to Oxidizer	Filtrate		6210 ⁴	4540	490	180	6.6	
	Solids		--	660	150	<5	<4	5220
	Total		--	5200	640	180	7	810
Thickener Feed								6030
	Filtrate		5980 ⁴	4240	600	58	3.9	
	Solids		--	310	74	<5	<4	4900
	Vent		--	ND ²	ND	ND	ND	380
	Total			4550	670	58	4	ND
								5280
Change Across Oxidizer								
	Filtrate		230 ⁴	300	-110	120	2.7	
	Solids		--	350	75	<5	<4	310
	Vent		--	ND	ND	ND	ND	420
	Total		--	650	-30	120	3	.3
								750

¹In mMoles of carbon per minute.

²ND = Not Detected.

³CO₂ in vent could not be distinguished between CaCO₃ decomposition and adipic acid degradation.

⁴Sum of adipic acid and glutaric acid.

TABLE 4-3. MATERIAL BALANCE AROUND OXIDIZER TANK (D-108) DURING SAMPLING RUN 2
(4/26/79; LOW OXIDATION CONDITIONS)

Process Stream	Sample Phase	By IC ¹		By GC Analysis ¹				By CO Monitor ¹	Total Carbon ¹	
		Adipic Acid	Adipic Acid	Adipic Acid	Glutaric Acid	Valeric Acid	Succinic Acid	Carbon Monoxide	By GC w/o CO ₂ Included ³	
Bleed to Oxidizer	Filtrate	5570		4110	350	80	5.7	--	4550	
	Solids	--		210	70	<5	<4	--	280	
	Total	--		4320	420	80	6	--	4830	
Thickener Feed	Filtrate	5300		3970	420	<5	<4	--	4390	
	Solids	--		63	30	<5	<4	--	90	
	Vent			ND ²	ND	ND	ND	.3	.3	
	Total			4030	450	<5	<4	.3	4480	
Change Across Oxidizer	Filtrate	270		140	-70	80	6	--	160	
	Solids	--		150	40	<5	<4	--	190	
	Vent			ND	ND	ND	ND	.3	.3	
	Total			290	-30	80	6	.3	350	

¹In mMoles of carbon per minute.

²ND = Not Detected.

³CO₂ in vent could not be distinguished between CaCO₃ decomposition and adipic acid degradation.

TABLE 4-4. MATERIAL BALANCE AROUND OXIDIZER TANK (D-108) DURING SAMPLING RUN 3
(4/27/79; HIGH OXIDATION CONDITIONS)

Process Stream	Sample Phase	By IC ¹				By GC Analysis ¹				By CO Monitor ¹	Total Carbon ¹	
		Adipic Acid	Adipic Acid	Adipic Acid	Adipic Acid	Glutaric Acid	Valeric Acid	Succinic Acid	Carbon Monoxide	By GC w/o CO ₂ Included ³		
Bleed to Oxidizer	Filtrate	3910	2560			220	30	9.6	--		2820	
	Solids	--	70			20	<5	<5	--		90	
	Total		2630			240	30	10	--		2910	
Thickener Feed	Filtrate	3750	2410			440	100	50	--		3000	
	Solids	--	15			5	<5	<5	--		20	
	Vent	--	ND ²			.004	.3	ND	7.1		7.4	
	Total		2420			440	100	50	7.1		3020	
Change Across Oxidizer	Filtrate	160	150			-220	-70	-40	--		-180	
	Solids	--	55			20	<5	<5	--		70	
	Vent	--	ND			0	0	ND	7.1		7.4	
	Total		210			-200	-70	-40	7.1		-110	

¹ In mMoles of carbon per minute.

² ND = Not Detected.

³ CO₂ in vent could not be distinguished between CaCO₃ decomposition and adipic acid degradation.

TABLE 4-5. MATERIAL BALANCE AROUND OXIDIZER TANK (D-108) DURING SAMPLING RUN 4
(4/27/79; HIGH OXIDATION CONDITIONS)

Process Stream	Sample Phase	By GC Analysis				By CO Monitor	Total Carbon By GC w/o CO ₂ Included ³
		By IC	Adipic ¹ Acid	Adipic ¹ Acid	Glutaric ¹ Acid	Valeric ¹ Acid	Succinic ¹ Acid
Bleed to Oxidizer	Filtrate	3900	2700	240	100	20	3060
	Solids	--	100	40	<5	<4	140
	Total	--	2800	280	100	20	3200
Thickener Feed	Filtrate	3890	2490	350	80	90	3010
	Solids	--	20	<4	<5	<4	20
	Vent	--	.04	.04	.12	ND ²	5
	Total		2510	350	80	90	3040
Change Across Oxidizer	Filtrate	110	210	-110	20	-70	50
	Solids	--	80	40	<5	<4	120
	Vent	--	.04	.04	.12	ND	5
	Total		290	-70	20	-70	160

¹In mMoles of carbon per minute.

²ND = Not Detected.

³CO₂ in vent could not be distinguished between CaCO₃ decomposition and adipic acid degradation.

A greater loss of adipic acid was unexpectedly observed across the oxidizer during the low oxidation conditions than during high oxidation. The quantities of organics found occluded with the solids decreased sharply as a function of the degree of oxidation. The fraction of adipic acid lost from the system by degradation across the oxidizer and with the filter cake is compared with the addition rate in Table 4-6. During low oxidation operation approximately 25 percent of the adipic acid added was degraded in the oxidizer but only 8 percent during the high oxidation tests. The unaccounted for adipic acid was either lost in other purge streams or degraded in other parts of the system.

While these results tend to be in conflict with earlier results indicating that higher degradation was associated with higher sulfite oxidation, other circumstances must be considered. The samples were collected during a period of upset. Namely, the pH had increased to nearly 7 during the night shift and efforts were being made to reduce this value to 5.5. As a result of the system not being at steady-state, accumulation or depletion of adipic acid may have been occurring in the oxidizer tank. Thus, while material balance estimates were calculated as shown in Table 4-6, the failure to account for all of the adipic acid losses may be due to these changing conditions. Another possible error to the balance calculation may be the variations in adipic acid concentrations as determined by the IC and GC techniques as seen in Tables 4-2, 4-3, and 4-4.

TABLE 4-6. SUMMARY OF ADIPIC ACID LOSSES FOUND DURING 4/26 AND 4/27/79

	Low Oxidation		High Oxidation	
	4/26	Percent	4/27	Percent
Adipic Acid Feed to Scrubber	6.2 lbs/hr	100	7.2 lbs/hr	100
Oxidizer Losses	1.6 lbs/hr	26	0.6 lbs/hr	8
Filter Cake Solids*	0.6 lbs/hr	10	0.6 lbs/hr	8
Filter Cake Liquor	2.4 lbs/hr	39	0.7 lbs/hr	10
Accounted For Losses		75		26

*Includes both adsorbed and occluded organics.

4.4 ANALYSIS OF SAMPLES FROM TCA

Slurry samples were taken from the TCA hold tank (D-204) on April 27 and 28, 1979, during Shawnee Run 901-2J. Analysis was performed on filtrates and solids for valeric, glutaric, and adipic acid. Filtrates were also analyzed

for sulfite content. Results are summarized in Table 4-7. The TCA samples were taken primarily to confirm the high sulfite values that had been measured by the on-site TVA personnel. High values were obtained from these samples as compared to earlier values of a few hundred mg/l. The occurrence of these higher sulfite values was apparently associated with a lowering of the scrubber slurry pH.

TABLE 4-7. ANALYTICAL RESULTS OF THE SHAWNEE TCA SAMPLES

Date	Time	Sample Point	Valeric Acid	Glutaric Acid	Adipic Acid	Sulfite
4/27	1315	D-204 Filtrate	74 mg/l	32 mg/l	1218 mg/l	1030 mg/l
4/28	1315	D-204 Filtrate	65 mg/l	12 mg/l	1201 mg/l	1621 mg/l
4/29	1315	D-204 Solids	ND ¹	102 µg/g	127 µg/g	---

¹Not Detected.

SECTION 5

LABORATORY TESTS

The laboratory degradation studies conducted previously by Radian indicate that the oxidation of sulfite in the presence of adipic acid was a necessary and sufficient condition for degradation to occur in a laboratory situation. Attempts to complete a material balance around the laboratory reactor system for adipic acid and its degradation products however were unsuccessful. The incomplete carbon balances suggested the possibility that not all of the degradation products had been identified. The laboratory tests conducted under the current program represent an attempt to further close the material balance around the bench scale system to assure that all degradation products have been identified.

5.1 METHODS

The bench-scale reactor system used in the current program was essentially the same as that which was previously used, with a few minor modifications and refinements. Basically, the system consisted of a reaction vessel followed by a series of traps for collection of gas phase species. The reaction vessel was a multi-necked, round bottom flask. Magnetic stirring was used to agitate the adipic-acid/calcium-sulfite slurry. Oxygen was supplied at a controlled flow rate and saturated by passing through an impinger of DI water prior to the reaction vessel. Both the reaction vessel and the water impinger were immersed in a water bath maintained at 50°C. The reaction vessel was equipped with a thermometer for monitoring the slurry temperature and a port for sample withdrawal. The reaction vessel and the preceding impinger of water generally comprised the complete system used in the screening tests. The test apparatus is diagrammed in Figure 5-1.

In the material balance tests, the off-gases from the reaction vessel were bubbled through two impingers of 1N sodium hydroxide solution. Both of these impingers were immersed in a cold bath maintained at 2°C. The sodium hydroxide impingers removed CO₂ and any volatilized or entrained acids from the gas stream as well as water vapor by condensation. The gas stream then passed through one or more solid sorbent traps designed to adsorb any hydrocarbon by-products. These traps consisted of lengths of 3/8" stainless steel tubing packed with silica gel and/or activated carbon and immersed in a cold bath at 5°C. A Mine Safety Appliances Model 70 carbon monoxide analyzer was used for measuring the CO concentration in the gas emerging from the hydrocarbon traps.

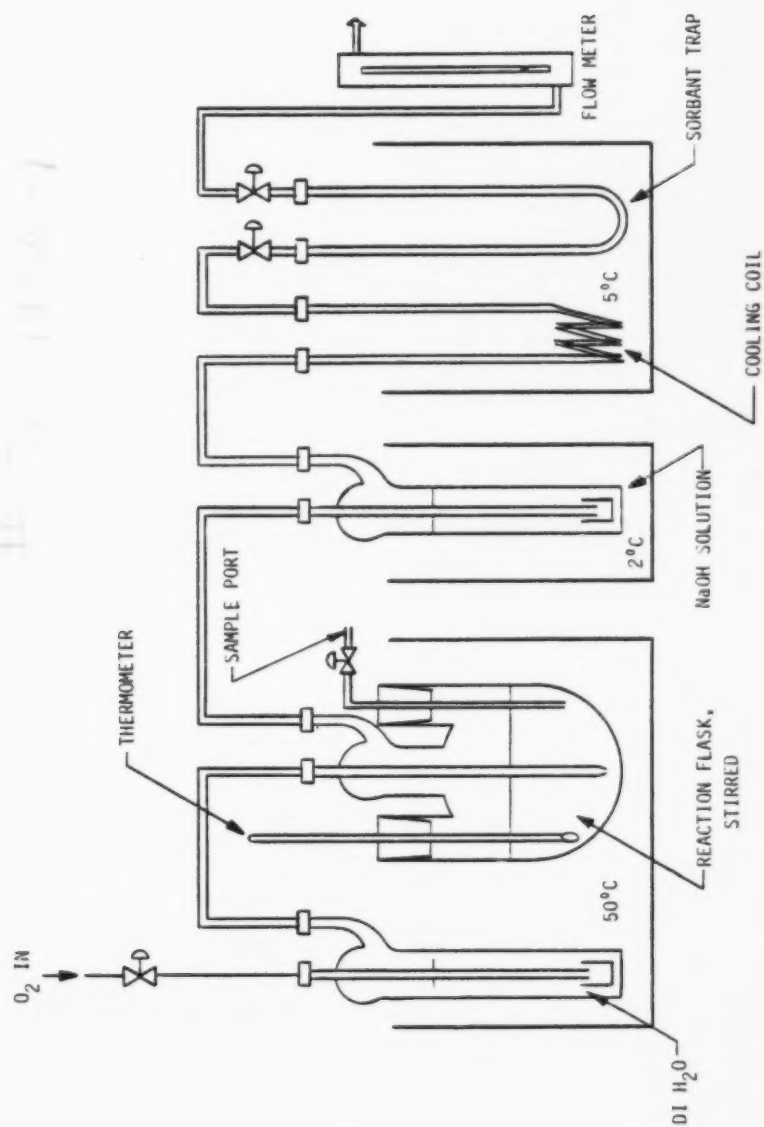


Figure 5-1. Laboratory apparatus for degradation tests with sorbent traps for gaseous species collection.

The laboratory degradation studies conducted in this program can be divided into two general categories: screening tests and material balance tests. The sampling and analytical schemes differed significantly for the two types of tests. In the screening tests, slurry samples were periodically withdrawn from the reaction vessel and separated into solid and liquid fractions. The liquid fraction was analyzed for adipic acid by IC; the sulfite concentration in the solid fraction was determined by iodometric titration. These data were used to assess the relative amounts of adipic acid degradation and sulfite oxidation in order to optimize the system prior to conducting the material balance experiments.

The sampling and analytical scheme for the material balance tests was considerably more involved. The samples taken during the material balance tests fall into four general classifications: blank, initial, intermediate and final samples.

The blank samples include all those analyzed to characterize the initial composition of various reagents and solutions. The 1500 ppm adipic acid solution used in the tests was analyzed repeatedly by IC and TOC. Samples of the solution were also carried through the extraction, concentration and esterification procedure (Appendix A) and analyzed by GC to characterize the efficiency of the procedure for the organic acid determinations. Adipic acid extracted from a sample of the starting solution was also analyzed by IR and the spectrum compared to that of the pure, dry solid. Samples from each batch of $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ prepared for use in the bench tests (Appendix B) were analyzed for SO_3 to determine their purity. A portion of the NaOH solution used in the gas traps was obtained before each test run and fixed in the same manner as the final samples that were analyzed for carbonate content. A sample of the NH_4 -EDTA solution used as the fixing agent was taken with each set of samples taken and analyzed to determine the blank value.

The initial samples for each test were withdrawn from the reaction vessel 15 minutes after it was placed in the water bath and stirring was initiated, but just before the oxygen purge was started. The sample was filtered and the solids were dried at 50°C and analyzed for sulfite. The filtrate was analyzed by IC and TOC. The intermediate samples were taken periodically during the test runs. Temperature and pH measurements were made immediately after sample removal, and at the conclusion of the test. Sample handling for the intermediate samples was essentially the same as that for initial samples, although analytical work was generally limited to IC analysis of the filtrate, with TOC and SO_3 analyses done only on selected samples.

The final samples for each test received the most intensive scrutiny. The most significant additions to the analytical scheme of the previous program were made to the analytical methods used to characterize the samples obtained at the conclusion of each test. These are also the most important samples, with respect to the material balance. The test slurry was filtered immediately upon conclusion of each run and the solids dried as before. The filtrate was divided into aliquots for IC, TOC and GC analysis as in the earlier program. In addition, a sample of filtrate was taken for non-dispersive IR analysis for carbonate determination. The final solids analytical

scheme also incorporates additions to that used in the previous degradation study. In addition to sulfite determinations and IR analyses, the solids were analyzed for carbonate by nondispersive IR. Also, using a refined extraction procedure (Appendix A), the adsorbed organics were recovered and quantified by GC. The sodium hydroxide solutions were divided into aliquots for CO₂ analysis and GC analysis for organic acids. The sorbant traps were thermally desorbed and analyzed by GC for C₁-C₄ hydrocarbons.

5.2 SCREENING TESTS

Material balance tests conducted as part of the previous program generally started with a 1500 ppm solution of adipic acid containing 5 grams of CaSO₃· $\frac{1}{2}$ H₂O solids per 100 ml of solution. In one test the starting concentration of adipic acid was 750 ppm. In each test the initial pH was adjusted to 6.0 with NaOH.

Before starting the material balance testing for the current project, a series of screening tests was conducted to assess the impact of certain variables upon adipic acid degradation and sulfite oxidation, and the extent to which the reactions proceed in a given period of time. The screening tests were set up in essentially the same manner as the material balance tests. The main difference between the two was in the sampling and analytical schemes employed. No gas traps were used downstream of the reaction vessel in most of the screening tests, thus eliminating all associated analyses. Samples were periodically removed from the reaction vessel and separated by filtration into solid and liquid fractions. The filtrates were analyzed for adipic acid and the solids for sulfite. These values were sufficient to reflect the relative extent of degradation and sulfite oxidation which had occurred.

The tests in the earlier program showed approximately a 50 to 1 mole ratio of sulfite oxidation to adipic acid degradation. Conditions for the first test were based on this ratio, aiming for 50% degradation with 100% sulfite oxidation. The test was run using a 2000 ppm solution of adipic acid and 5.5 grams of 80% calcium sulfite per 100 ml of solution. The pH was adjusted to 6.0 and oxygen flow was set at 20 ml/min. After 20 hours, only 21% of the sulfite in the solids had been oxidized. Due to problems with the apparatus, mixing of the test slurry during the run was very poor casting doubt on the validity of the results. A second run was made under the same conditions to obtain more reliable data. After 23 hours, only 8% of the solid sulfite had been oxidized and adipic acid degradation was only about 10%. After 88 hours, oxidation was approximately 20% and degradation approximately 18%. The results of this test are summarized in Table 5-1.

The third screening test was run under the same conditions as the first two except that the amount of solids used was reduced by one half, using 2.75 grams per 100 ml of solution. In this test approximately 85% of the calcium sulfite was oxidized to sulfate after 18 hours and the corresponding

TABLE 5-1. SUMMARY OF RESULTS FOR SCREENING TEST #2¹

Sample	Elapsed Time (Hours)	pH ²	Adipic Acid Concentration (ppm)	Adipic Acid Concentration $\Delta\%$ From Start	% SO ₃ = Oxidation
1	16	--	1840	8	NA ³
2	23	--	1790	11	8
3	73	--	1670	17	NA
4	88	--	1650	18	20

¹ 300 ml 2000 ppm adipic acid plus 16.5 g 80% CaSO₃· $\frac{1}{2}$ H₂O, pH 6.0, 20 ml O₂/min for 88 hours at 50°C.

² pH values obtained were erroneous due to bad electrode.

³ Not analyzed.

decrease in adipic acid concentration was about 24%. Results for this test are presented in Table 5-2.

In the next screening test the pH of the solution was not adjusted to 6.0 as in the other tests. After addition of the solids, the pH was measured and found to be 4.5. All other conditions were the same as in the first two tests: 2000 ppm adipic acid solution, 5.5 grams of 80% calcium sulfite solids per 100 ml of solution and 20 ml of oxygen per minute. In this test sulfite oxidation was comparable to that in the previous test on a molar basis. After 21.5 hours, 50% of the calcium sulfite was oxidized. After 38.5 hours, oxidation was about 95% and the change in adipic acid concentration indicates approximately 24% degradation. Test results are summarized in Table 5-3.

The fifth test was run under essentially the same conditions as the preceding test: 5.5 grams of 80% $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ per 100 ml of 2000 ppm adipic acid solution, with 20 ml/min oxygen flow and no pH adjustment. The only difference between the two tests was the addition in this case of the NaOH impingers and hydrocarbon traps downstream of the reaction vessel. While the rate of sulfite oxidation was very near that seen in the previous test, the observed adipic acid degradation was quite different. The results for this test are summarized in Table 5-4.

In order to demonstrate that the observed decrease in adipic acid concentration between the first two samples in this test was due, at least in part, to something other than degradation, a test was done under conditions such that little or no degradation would be expected. This was accomplished by running the test in a sealed reaction vessel with no oxygen purge. Only a very small amount of oxygen, that contained in the headspace, would then be available for sulfite oxidation, thus hopefully reducing the degradation process. The same volume of 2000 ppm adipic acid and same quantity of solids were used as in the previous test. Once again no pH adjustment was made. Sample removal was accomplished without allowing additional air into the vessel. No pH measurements were made concurrent with sample withdrawal because to do so would have necessitated opening the vessel. As can be seen in Table 5-5, a significant decrease in adipic acid concentration in the filtrate occurred in the first 15 minutes of the test. An increase was observed over the next several hours with the concentration finally reaching a value which is essentially the same as the initial concentration. Since there is virtually no difference between the initial and final concentrations, it is reasonable to conclude that degradation did not take place. This would indicate that the observed decrease and subsequent increase in concentration of adipic acid in the filtrate must be due to some process other than degradation. Detailed characterization of solids from subsequent material balance tests indicates that substantial amounts of adipic acid may be adsorbed by the unoxidized solids. This absorption process seems to be the most plausible explanation for the observed changes in adipic concentration in this test.

TABLE 5-2. SUMMARY OF RESULTS FOR SCREENING TEST #3¹

Sample	Elapsed Time (Hours)	pH	Adipic Acid Concentration (ppm)	Adipic Acid Concentration $\Delta\%$ From Start	% SO ₃ ⁻ Oxidation
1	2.0	5.3	1940	3	5.6
2	18.0	6.1	1530	24	85
3	24.5	6.7	1390	31	NA ²

¹ 300 ml 2000 ppm adipic acid plus 8.25 g 80% CaSO₃· $\frac{1}{2}$ H₂O, pH 6.0, 20 ml O₂/min for 24.5 hours at 50°C.

² Not analyzed.

TABLE 5-3. SUMMARY OF RESULTS FOR SCREENING TEST #4¹

Sample	Elapsed Time (Hours)	pH	Adipic Acid Concentration (ppm)	Adipic Acid Concentration $\Delta\%$ From Start	% SO ₃ ⁻ Oxidation
1	15.5	4.5	1710	15	30
2	21.5	4.5	NA ²	--	50
3	38.5	4.1	1520	24	95

¹ 300 ml 2000 ppm adipic acid plus 16.5 g 80% CaSO₃· $\frac{1}{2}$ H₂O, pH 4.5, 20 ml O₂/min for 38.5 hours at 50°C.

² Not analyzed.

TABLE 5-4. SUMMARY OF RESULTS FOR SCREENING TEST #5¹

Sample	Elapsed Time (Hours)	pH	Adipic Acid Concentration (ppm)	Adipic Acid Concentration $\Delta\%$ From Start	% SO ₃ ⁼ Oxidation
1	20.5	4.4	1820	9	55
2	24.5		1490	26	63
3	27.0	4.5	1830 ²	9	71

¹ 300 ml 2000 ppm adipic acid plus 16.5 g 80% CaSO₃· $\frac{1}{2}$ H₂O, pH 4.5, 20 ml O₂/min for 27 hours at 50°C.

² Possible analytical error.

TABLE 5-5. SUMMARY OF RESULTS FOR SCREENING TEST #6¹

Sample	Elapsed Time (Hrs)	Adipic Acid Conc (ppm)	Adipic Conc Δ % From Start
1	0.25	1840	8
2	2.25	1890	6
3	4.25	1890	6
4	20.0	1990	1

¹ 300 ml 2000 ppm adipic acid plus 16.5 g 80% $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, pH 4.5, no purge, 20 hr duration.

5.3 MATERIAL BALANCE TESTS

The limited number of screening tests which were performed did not succeed in establishing a set of conditions under which 50% of the adipic acid was degraded during the course of a run. Rather than continue searching for optimum experimental conditions, time constraints dictated that material balance testing be initiated without further delay. Since no new conditions were found to be significantly better for experimental purposes than the conditions established in the earlier program, these conditions were chosen as the basis for the material balance tests. This consistency provided one advantage in that data from the new tests are more easily compared to that obtained in the earlier test program.

The first material balance test was run under essentially the same set of conditions as used in the initial program. The initial adipic acid concentration was 1500 ppm and 300 ml of solution was used. Five grams of 93% calcium sulfite was added for each 100 ml of solution for a total of 15 grams of solids. After addition of the solids, the pH of the test solution was adjusted to 6.0 with NaOH. The first CO₂ trap contained 150 ml of 1 N NaOH and the second contained 100 ml. The hydrocarbon traps used for this test were arranged in a manner aimed at providing an indication of whether or not breakthrough was occurring, and if so, to what extent. Three traps were used for the first hour of the test. One activated carbon trap and two silica gel traps were used, with the carbon trap second in line. After the first hour, all three traps were removed and replaced by a single silica gel trap which remained in line for the duration of the 24 hour run. The gas emerging from the hydrocarbon traps was continuously monitored for carbon monoxide using a Mine Safety Appliances CO analyzer. The results of this test are presented in Table 5-6. Only trace amounts (<2 ppm) of CO were detected during the run, representing an insignificant amount of material with respect to the material balance. Material balance results for the Test #1 are presented in Table 5-7.

The second material balance test was intended to be a confirmation run duplicating the previous test. The only significant difference in operating conditions was the use of a new batch of CaSO₃· $\frac{1}{2}$ H₂O solids. These solids were analyzed and found to be 99.2% CaSO₃· $\frac{1}{2}$ H₂O by weight. No indication of hydrocarbon breakthrough was observed during the previous test, therefore, a single silica gel trap was used for this test. The test duration was again 24 hours. The results of this test are summarized in Table 5-8. Material balance calculations using this data are presented in Table 5-9.

Although the first two tests were intended to be duplicate runs under the same conditions, the results of the two tests are quite dissimilar. The most obvious difference is that significantly less of the lost adipic acid is accounted for in the second test. Furthermore, there is a marked shift in relative amounts of valeric and glutaric acid in the liquid phase. This is accompanied by a pronounced difference in the amount of adsorbed adipic acid in the solids. Time constraints precluded the intensive investigation which would be required to resolve the observed inconsistencies.

TABLE 5-6. SUMMARY OF ANALYTICAL RESULTS FOR FINAL SAMPLES,
MATERIAL BALANCE TEST #1--STANDARD CONDITIONS¹

	Adipic Acid ² (ppm)	Valeric Acid ³ (ppm)	Glutaric Acid ³ (ppm)	Carbon Dioxide (mmoles)	Carbonate (ppm)	Hydrocarbons (ppm)	ASO ₃ (mmoles)
Liquid	1280	2.65	18	.050	57	.127	--
				--	--	20	.09
Solid	840	.09	25	.004	7	.001	--
				--	--	720	.19
Gas	2	.002	<1	<.001	<1	<.001	330
				--	--	.41	--
						C ₁ = .76	<.001
						C ₂ = .01	<.001
						C ₃ = .03	<.001
						C ₄ = .02	<.001

¹ 300 ml 1500 ppm adipic acid plus 15g 93% CaSO₃, 1/2 H₂O,
pH 6.0, 20 ml O₂/min for 24 hrs. at 50°C

² Determined by IC Analysis

³ Determined by GC Analysis

TABLE 5-7. CARBON BALANCE FOR MATERIAL BALANCE TEST #1
--STANDARD CONDITIONS

	Initial		Final						
	Adipic Acid (mMoles C)	Adipic Acid (mMoles C)	Valeric Acid (mMoles C)	Glutaric Acid (mMoles C)	Carbon Dioxide (mMoles C)	Carbonate (mMoles C)	Hydrocarbons (mMoles C)	Carbon Monoxide (mMoles C)	Fraction of Lost Adipic Acid ¹
Liquid	18.49	15.91	.25	.64	--	.09	--	--	38%
Solid	0	.54	.02	.01	--	.19	--	--	29%
Gas	0	.01	<.01	<.01	.42	--	<.01	<.01	17%
Total	18.49	16.46	.27	.65	.42	.28	<.01	<.01	84%

¹ Percent of 'missing' adipic acid accounted for at conclusion of test.

i.e., $\frac{\% \text{ degradation products and adsorbed adipic acid (mMoles C)}}{\text{Initial adipic acid in liquid} - \text{final adipic acid in liquid (mMoles C)}} \times 100$

TABLE 5-8. SUMMARY OF ANALYTICAL RESULTS FOR FINAL SAMPLES.
MATERIAL BALANCE TEST #2--STANDARD CONDITIONS¹

	Adipic Acid ² (ppm)	Valeric Acid ³ (ppm)	Glutaric Acid ³ (ppm)	Carbon Dioxide (mMoles)	Carbonate (ppm)	Hydrocarbons (ppm)	Hydrocarbons (mMoles)	ΔSO_3 (mMoles)			
Liquid	1270	2.65	31	.086	21.3	.045	--	10	.05	--	--
Solid	330	.037	32	.01	<1	<.001	--	660	.18	--	30.1
Gas ³	1	.001	<1	<.001	<1	<.001	365	.47	--	--	C ₁ =1.00 C ₂ =0.06 C ₃ =0.05 C ₄ =0.52

¹ 300 ml 1500 ppm adipic acid plus 15g 99% CaSO₃, 1/2 H₂O,
pH 6.0, 20 ml O₂/min for 24 hrs at 50°C

² Determined by IC Analysis

³ Determined by GC Analysis

TABLE 5-9. CARBON BALANCE FOR MATERIAL. BALANCE TEST #2
--STANDARD CONDITIONS

	Initial		Final						Fraction of 'Lost', Adipic Acid ¹
	Adipic Acid (moles C)	Adipic Acid (moles C)	Valeric Acid (moles C)	Glutaric Acid (moles C)	Carbon Dioxide (moles C)	Carbonate (moles C)	Hydrocarbons (moles C)	Carbon Monoxide (moles C)	
Liquid	18.49	15.91	.43	.23	--	.05	--	--	28%
Solid	0	.22	.03	<.01	--	.18	--	--	17%
Gas	0	.01	<.01	<.01	.47	--	<.01	<.01	19%
Total	18.49	16.14	.46	.23	.47	.23	<.01	<.01	63%

Percent of 'missing' adipic acid accounted for at conclusion of test,

Expt. no.	Y. degradation products and adsorbed adipic acid (moles C)		Initial adipic acid in liquid - final adipic acid in liquid (moles C) $\times 100$
	Initial	Final	
1	0.00	0.00	0.0
2	0.00	0.00	0.0
3	0.00	0.00	0.0
4	0.00	0.00	0.0
5	0.00	0.00	0.0
6	0.00	0.00	0.0
7	0.00	0.00	0.0
8	0.00	0.00	0.0
9	0.00	0.00	0.0
10	0.00	0.00	0.0
11	0.00	0.00	0.0
12	0.00	0.00	0.0
13	0.00	0.00	0.0
14	0.00	0.00	0.0
15	0.00	0.00	0.0
16	0.00	0.00	0.0
17	0.00	0.00	0.0
18	0.00	0.00	0.0
19	0.00	0.00	0.0
20	0.00	0.00	0.0
21	0.00	0.00	0.0
22	0.00	0.00	0.0
23	0.00	0.00	0.0
24	0.00	0.00	0.0
25	0.00	0.00	0.0
26	0.00	0.00	0.0
27	0.00	0.00	0.0
28	0.00	0.00	0.0
29	0.00	0.00	0.0
30	0.00	0.00	0.0
31	0.00	0.00	0.0
32	0.00	0.00	0.0
33	0.00	0.00	0.0
34	0.00	0.00	0.0
35	0.00	0.00	0.0
36	0.00	0.00	0.0
37	0.00	0.00	0.0
38	0.00	0.00	0.0
39	0.00	0.00	0.0
40	0.00	0.00	0.0
41	0.00	0.00	0.0
42	0.00	0.00	0.0
43	0.00	0.00	0.0
44	0.00	0.00	0.0
45	0.00	0.00	0.0
46	0.00	0.00	0.0
47	0.00	0.00	0.0
48	0.00	0.00	0.0
49	0.00	0.00	0.0
50	0.00	0.00	0.0
51	0.00	0.00	0.0
52	0.00	0.00	0.0
53	0.00	0.00	0.0
54	0.00	0.00	0.0
55	0.00	0.00	0.0
56	0.00	0.00	0.0
57	0.00	0.00	0.0
58	0.00	0.00	0.0
59	0.00	0.00	0.0
60	0.00	0.00	0.0
61	0.00	0.00	0.0
62	0.00	0.00	0.0
63	0.00	0.00	0.0
64	0.00	0.00	0.0
65	0.00	0.00	0.0
66	0.00	0.00	0.0
67	0.00	0.00	0.0
68	0.00	0.00	0.0
69	0.00	0.00	0.0
70	0.00	0.00	0.0
71	0.00	0.00	0.0
72	0.00	0.00	0.0
73	0.00	0.00	0.0
74	0.00	0.00	0.0
75	0.00	0.00	0.0
76	0.00	0.00	0.0
77	0.00	0.00	0.0
78	0.00	0.00	0.0
79	0.00	0.00	0.0
80	0.00	0.00	0.0
81	0.00	0.00	0.0
82	0.00	0.00	0.0
83	0.00	0.00	0.0
84	0.00	0.00	0.0
85	0.00	0.00	0.0
86	0.00	0.00	0.0
87	0.00	0.00	0.0
88	0.00	0.00	0.0
89	0.00	0.00	0.0
90	0.00	0.00	0.0
91	0.00	0.00	

The third material balance test differed from the second in two respects. First, the test duration was only six hours rather than 24. Second, the oxygen flow rate was controlled at 40 ml/min, twice that of the previous tests. Continuous monitoring of CO in the gas stream was discontinued since data from the first two tests indicated amounts too small to have a significant effect on the material balance.

If available oxygen was a limiting factor in the previous tests, the degradation rate would be expected to increase as a function of the increase in oxygen flow rate. The test results, presented in Table 5-10, indicate that increasing the O₂ purge rate had no appreciable effect upon the degradation rate. The adipic acid loss for this test was virtually the same as that which occurred during the first six hours of the previous tests.

Table 5-11 presents the material balance calculated for this test. Apparently, all degradation products are accounted for, within the bounds of analytical error. Once again, a significant change in the distribution of by-products is seen. However, in light of the differences seen between the first two tests in which operating conditions were supposedly the same, any cause-effect relationships which might be indicated will require more extensive validation than provided by data from a single test.

The final material balance test was of six hours duration as was the previous run. All test conditions were the same as those in the second material balance test, with two exceptions. The solids used in this test were from a new batch assayed as 96% CaSO₃· $\frac{1}{2}$ H₂O by weight. The major difference, however, was the addition of 2.75 grams of anhydrous Na₂SO₄ to the test solution volume. The very high solubility of Na₂SO₄ results in a high SO₄⁼ concentration which tends to lower the solubility of CaSO₄·2H₂O by the common ion effect. The resulting low calcium concentration in turn increases the solubility of CaSO₄· $\frac{1}{2}$ H₂O resulting in a higher liquid phase concentration of SO₃⁼. The higher sulfite concentration should result in a lower free radical concentration and thereby reduce the attack on adipic acid.

The results of this test are summarized in Table 5-12. Corresponding material balance calculations appear in Table 5-13.

Although slightly more degradation was seen in this test than in the first three, the difference is too small to be taken as conclusive evidence of a significant rate change. Additional experimental work would be necessary to fully assess the impact of SO₃⁼ concentration on the rate of adipic acid degradation.

While the material balance closure for this test is not as good as that achieved in the first and third test, several aspects of the data are noteworthy. The pronounced decreases and subsequent increases in filtrate adipic acid concentrations seen in the other material balance tests are especially large in this case. Also seen in this test, and in the previous

TABLE 5-10. SUMMARY OF ANALYTICAL RESULTS FOR FINAL SAMPLES,
MATERIAL BALANCE TEST #3--HIGH PURGE RATE¹

	Adipic Acid ² (ppm)	Valeric Acid ³ (ppm)	Glutaric Acid ³ (ppm)	Carbon Dioxide (mMoles)	Carbonate (ppm) (mMoles)	Hydrocarbons (ppm) (mMoles)	ΔSO ₃ mMoles
Liquid	1290	2.71	67	.191	2	.004	--
				--	--	.10	--
Solid	440	.049	52	.008	6	.001	--
				--	--	.20	--
Gas	43	.028	3	.002	<1	<.001	32.0
					264	.41	--
						C ₁ =1.59	.001
						C ₂ = .04	<.001
						C ₃ = .13	<.001
						C ₄ =2.33	.001

¹ 300 ml 1500 ppm adipic acid plus 15g 99% CaSO₃ · 1/2 H₂O,
pH 6.0, 40 ml O₂/min for 6 hrs. at 50°C

² Determined by IC Analysis

³ Determined by GC Analysis

TABLE 5-11. CARBON BALANCE FOR MATERIAL BALANCE TEST #3
--HIGH PURGE RATE

	Initial		Final						Fraction of 'Lost' Adipic Acid ¹
	Adipic Acid (moles C)	Adipic Acid (moles C)	Valeric Acid (moles C)	Glutaric Acid (moles C)	Carbon Dioxide (moles C)	Carbon- ate (moles C)	Hydro- carbons (moles C)	Carbon Monoxide (moles C)	
Liquid	18.49	16.27	.95	.02	--	.10	--	--	48%
Solid	0	.29	.04	.01	--	.20	--	--	24%
Gas	0	.16	.01	<.01	.41	--	.01	NA ²	27%
Total	18.49	16.72	1.00	.03	.41	.30	.01	--	99%

¹ Percent of 'missing' adipic acid accounted for at conclusion of test,

i.e., $\frac{\sum \text{degradation products and adsorbed adipic acid (moles C)}}{\text{Initial adipic acid in liquid} - \text{final adipic acid in liquid (moles C)}} \times 100$

² Not Analyzed

TABLE 5-12. SUMMARY OF ANALYTICAL RESULTS FOR FINAL SAMPLES,
MATERIAL BALANCE TEST #4--SODIUM SULFATE ADDITION¹

	Adipic Acid ² (ppm)	Valeric Acid ³ (ppm)	Glutaric Acid ³ (ppm)	Carbon Dioxide (mMoles)	Carbonate (ppm)	Hydrocarbons (ppm)	ΔSO_3 (mMoles)
Liquid	1300	2.61	74	.197	<1	<.001	--
						4	.02
Solid	360	.037	27	.004	<1	<.001	--
						680	.17
Gas ⁴	65	.021	<1	<.001	<1	<.001	--
						841	.27
						--	NA ⁴
						--	NA

¹ 300 ml 1500 ppm adipic acid, 15g 96% CaSO₃ + 1/2 H₂O plus 2.75g Na₂SO₄,
pH 6.0, 20 ml O₂/min for 6 hrs at 50°C

² Determined by IC Analysis

³ Determined by GC Analysis

⁴ Not Analyzed

TABLE 5-13. CARBON BALANCE FOR MATERIAL BALANCE TEST #4
--SODIUM SULFATE ADDITION

	Initial		Final						
	Adipic Acid (mMoles C)	Adipic Acid (mMoles C)	Valeric Acid (mMoles C)	Glutaric Acid (mMoles C)	Carbon Dioxide (mMoles C)	Carbonate (mMoles C)	Hydrocarbons (mMoles C)	Carbon Monoxide (mMoles C)	Fraction of 'Lost' Adipic Acid ¹
Liquid	18.49	15.67	.99	<.01	--	.02	--	--	36%
Solid	0	.22	.02	<.01	--	.17	--	--	15%
Gas	0	.13	<.01	<.01	.27	--	NA ²	NA	14%
Total	18.49	16.02	1.01	<.01	.27	.19	--	--	65%

¹ Percent of 'missing' adipic acid accounted for at conclusion of test,

i.e., $\frac{\% \text{ degradation products and adsorbed adipic acid (mMoles C)}}{\text{Initial adipic acid in liquid} - \text{final adipic acid in liquid (mMoles C)}} \times 100$

² Not Analyzed

test, is a significant shift from glutaric acid to valeric acid as a major by-product of the degradation process. The quantity of CO₂ collected in this test is also considerably less than that of the first three tests, as indicated in Table 5-12. A summary of the adipic acid concentrations at the various tests conditions is given in Table 5-14.

As in the last two screening tests, the adipic acid concentrations observed in the material balance tests exhibit changes which are not wholly attributable to degradation. For the purpose of calculating material balances in the foregoing tests, degradation is calculated from the net change in liquid phase adipic acid concentration as measured by IC. Allowances are made in the calculations for sample removal during the tests.

The material balances achieved in this series of tests represent a significant improvement over those conducted previously. The extensive solids characterizations conducted as part of these tests are largely responsible for the improvement. Carbonate and adsorbed adipic acid made significant contributions in each material balance. TOC analyses of filtrate samples from the bench tests seem quite consistent with values calculated from IC and GC data, as seen in Table 5-15. This tends to support the relatively good material balance data, indicating that all by-products of degradation in the bench tests have been identified. Although the laboratory tests do not precisely duplicate all processes which occur in an aqueous FGD system, they do provide valuable insight into phenomena associated with the use of adipic acid in such systems.

TABLE 5-14. MATERIAL BALANCE TESTS--CHANGES IN ADIPIC
ACID CONCENTRATION AND pH OVER TEST DURATION

Test	Sample	Elapsed Time (Hrs)	pH	Adipic Acid By IC (ppm)
#1	1	0.25	-	1400
Standard	2	1.25	5.7	1140
Conditions	3	3.25	5.6	1260
	4	6.25	5.6	1330
	5	24.25	6.1	1280
#2	1	0.25	5.9	1280
Standard	2	1.25	5.7	1260
Conditions	3	3.25	5.6	1240
	4	5.25	5.7	1260
	5	6.25	5.8	1370
	6	24.25	6.3	1270
#3	1	0.25	-	1450
High O ₂	2	1.25	5.3	1310
Purge Rate	3	3.25	5.4	1440
	4	6.25	5.6	1290
#4	1	0.25	-	1240
Na ₂ SO ₄	2	1.25	5.6	1060
Addition	3	3.25	5.5	1070
	4	6.25	5.6	1300

¹ Initial adipic acid concentration was 1500 ppm in all tests.

TABLE 5-15. COMPARISON OF TOC, IC AND GC VALUES FOR ORGANIC CARBON IN MATERIAL BALANCE TESTS

Test	Sample Designation	TOC (m Moles C/l)	IC (m Moles C/l)	GC ¹ (m Moles C/l)
#1 - Standard Conditions	Initial	59.1	57.5 ²	NA ⁴
	Final	60.2	55.7 ³	61.2
#2 - Standard Conditions	Initial	47.0	52.6 ²	NA
	Final	56.0	54.5 ³	54.6
#3 - High O ₂ Purge Rate	Initial	58.6	59.6 ²	NA
	Final	53.2	56.4 ³	48.6
#4 - Na ₂ SO ₄ Addition	Initial	NA	51.0 ²	NA
	Final	61.1	57.0 ³	58.9

¹ Millimoles of organic carbon per liter calculated using GC values for all organic species detected in liquid phase.

² Millimoles of organic carbon per liter calculated using only IC values for adipic acid concentration--GC values for other organic species not available.

³ Millimoles of organic carbon per liter calculated using IC value for adipic acid concentration and GC values for other organic species in liquid phase.

⁴ Not Analyzed.

SECTION 6

SOLIDS CHARACTERIZATION

A digestion and analytical scheme has been used to identify and quantify the organic content of the Shawnee and bench scale solids for material balance testing and to determine the form of adipic acid in the solid, i.e., occluded, adsorbed, etc. Details of the procedure are presented in this section.

6.1 ANALYTICAL PROCEDURE

A predetermined quantity of the dried scrubber solid is accurately weighed, then stirred in a 10 percent sulfuric acid solution for one-half hour. The synthetic scrubber solids generated from bench scale testing were found to completely dissolve; however, due to the presence of fly ash in the actual scrubber solids, total dissolution was not achieved. This does not pose a problem since adipic acid and its degradation products would not be occluded in the insoluble portions.

After digestion the solution and any undissolved solids are extracted with ether. Then the ether fraction is separated and concentrated by evaporation. The concentrate is analyzed by gas chromatography using the same procedure used for liquid samples.

In order to achieve a detection limit of 10 $\mu\text{g/g}$ for adipic, glutaric and valeric acids, it is necessary to concentrate the ether extract to a high degree. Usually 750 ml of ether are concentrated to 1 ml. All impurities in the ether used for extraction are concentrated to the same degree as the extracted acids. As a result, the chromatograms obtained during GC analyses of the concentrated extracts contain many extraneous peaks. A typical solids blank and a typical solids sample are shown in Appendix C. The extraneous peaks do not directly interfere with the identity of the compounds, but can cause some error in the determination of the concentrations. Using comparison of the samples and standards on a peak height basis as opposed to an integrated area reduces these errors.

The previous material balance attempts around the pilot scrubbers at RTP and Shawnee failed to determine what happened to all of the adipic acid that was added to the systems. Inspection of the flow rates of the various discharge streams indicates the 300 to 3000 ppm of adipic acid in the solids would account for the missing fraction. Since the method used to analyze the

solids collected during these material balance sampling efforts was found to have a detection limit no better than 1000 ppm, an alternate technique was used to quantify the adipic and other carboxylic acids content in the solids. Sample aliquots were chosen to attain a detection limit of 10 ppm.

6.2 ANALYSIS OF SHAWNEE SCRUBBER SOLIDS

Most of the solids collected from the Shawnee venturi/spray tower scrubber were washed thoroughly with deionized water to remove any adherent scrubber solution. The solids were then dried and subjected to the previously described procedure. The results of these determinations are included in the data in Tables 4-2 through 4-5. The concentrations of carboxylic acids in the solids varies considerably from sample to sample even though the corresponding solution compositions are fairly uniform. The only trend noticeable appears to be a correlation between the amount of organics and the degree of oxidation. The high sulfite containing solids seem to incorporate a higher concentration of organics.

The ratio of adipic acid to glutaric acid in the solids differs from that ratio in the liquid phase (see Table 6-1). The ratio is about 9:1 in the liquid, but only 3:1 in the solids.

The amount of adipic and glutaric acids in the "low oxidation" solids is sufficient to account for the missing quantities during the low oxidation tests at RTP. However, the loss rate of adipic acid increases substantially during forced oxidation as observed at both RTP and Shawnee. On the other hand, the amount of organics coprecipitated with the solids decreases below 50 ppm during forced oxidation and, therefore, accounts for only a small fraction of the lost adipic acid. The possibility of adsorption on the surface of the solids, however, cannot be ruled out.

6.3 ANALYSIS OF LABORATORY TEST SOLIDS

The adsorption of adipic acid on the surface of the Shawnee scrubber solids collected during this program could not be determined since the solids were thoroughly washed prior to analysis. However, the solids generated in the bench scale tests were treated in a manner that both adsorbed and occluded organics could be determined. A sample of the filter cake collected with the Shawnee scrubber samples was also analyzed in this manner.

The fraction of organic occluded with the solids collected at the conclusion of two of the laboratory tests was determined by analyzing the washed samples. The solids were dissolved and the organics extracted and determined by GC. No organic acids could be detected in these samples.

The fraction of organics adsorbed to the surface of the solids was determined by first drying the solids separated from the test solution. The solids in this case were not washed to remove to adherent solution. The dried samples were then analyzed for organic acids as described previously. The quantity of adherent solution was determined by measuring the sodium concentration in

TABLE 6-1. RELATIVE LEVELS OF ADIPIC ACID AND GLUTARIC ACID IN SCRUBBER SOLIDS
(Concentrations in ppm)

Run	Sample Points	pH	Temp (°C)	Adipic Acid in Solids	Glutaric Acid in Solids	$\frac{[\text{Adipic Acid}]}{[\text{Glutaric Acid}]}$ in Solids	$\frac{[\text{Adipic Acid}]}{[\text{Glutaric Acid}]}$ in Filtrate	Tendency of Glutaric Acid to Occlude Relative to Adipic Acid ¹
1	Oxidizer Bleed	5.8	NA ²	815	203	4.00	10.3	2.58
1	Thickener Feed	7.1	NA	377	99	3.81	8.4	2.20
2	Oxidizer Bleed	5.7	48	260	98	2.65	10.8	4.08
2	Thickener Feed	7.1	44	78	41	1.90	8.8	4.63
3	Oxidizer Bleed	5.8	51	147	41	3.59	10.7	2.98
3	Thickener Feed	5.2	61	27	<10	>2.7	5.1	<2
4	Oxidizer Bleed	5.5	50	197	81	2.43	10.3	4.23
4	Thickener Feed	5.5	64	40	<10	>4	6.5	1.62
AVERAGE						3.14 ± .81	8.86 ± 2.11	3.02 ± 1.15

²Not Available.

the solution obtained by dissolving the solids. This value was corrected for the quantity of sodium found in the washed samples. The results of these measurements are shown in Table 6-2.

The concentrations of sodium in the filtrate and the washed and unwashed solids were used to calculate the quantity of solution that was associated with the unwashed solids prior to drying. During the drying of the solid samples it was assumed that only water was lost. It was also assumed that no appreciable amount of sodium was adsorbed to the surface of the solids.

Similar calculations were carried out using the organic concentrations measured in the solution and solids to estimate the quantities that were apparently adsorbed to the surfaces of the solids. Approximately 500 μg of adipic acid per gram of solids appear to be associated with the solids due to adsorption. While this amount, if the same phenomenon occurs in the pilot studies, would only represent about 20 to 30% of the unaccounted adipic acid, measurements to accurately determine the adsorbed fraction of organics on the field samples are definitely recommended.

No measureable quantities of organics were found in the washed solids from the fully oxidized solids generated during the laboratory studies. This supports the low concentrations observed in the highly oxidized field samples. The quantities of organics occluded with the scrubber solids appear to be associated with the $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ fraction.

TABLE 6-2. RELATIVE CONTRIBUTIONS OF OCCLUSION, ADSORPTION, AND EVAPORATIVE DEPOSITION TO ADIPIC ACID AND VALERIC ACID LEVELS IN LABORATORY SCRUBBER SOLIDS¹

	ML.S		Sodium		Adipic Acid		Valeric Acid	
	A	B	A	B	A	B	A	B
Filtrate Concentration (µg/ml)			920	700	1270	1260	30	67
Unwashed Solids Concentration (µg/g)			1840	1880	840	930	64	103
Washed Solids Concentration (µg/g)	0.25	0.37	1660	1620	<10	<10	<10	<10
Volume of Filtrate Retained on 1 gram of solids (mla/g)	0.25	0.37						
Solids Concentration Due to Adsorption (µg/g)			0 ²	0 ²	520	460	56	78
Solids Concentration Due to Filtrate Retention (µg/g)					320	470	8	25
% Occluded					<1%	<1%	<20%	<10%
% Adsorbed			0 ²	0 ²	62%	49%	88%	76%
% Due to Filtrate Retention					38%	51%	12%	24%

¹ Two solid samples, designated A and B, were selected from the laboratory tests for this analysis.

² Assumed for purposes of calculation.

SECTION 7

EVALUATION OF ORGANIC ANALYTICAL DATA

Several analytical techniques have been used to characterize the organic components in the scrubber slurries during the addition of adipic acid. The concentrations of adipic acid and other lower carboxylic acids resulting from the degradation of adipic acid appear to be moderately consistent among the differentiating techniques. However, the total dissolved organics as measured by a standard total organic carbon (TOC) technique are generally higher in the field solutions than the sum of the individual components determined by the other specific methods. This difference was found to be as much as a factor of 2 in some samples.

In order to reconcile these differences, a series of analyses was carried out on field and laboratory test solutions. The procedures used to investigate this problem included:

- parallel GC, IC and TOC analyses on several Shawnee and laboratory test filtrates,
- TOC analyses of previously extracted filtrates,
- reduction of the extraction pH to less than 0.1,
- alkaline extractions, and
- gravimetric and infrared analyses of residues due to complete solvent evaporation on acidic ether extracts.

7.1 DIRECT COMPARISON OF ANALYTICAL RESULTS

The analytical results of the various methods used to study several samples are compared in Table 7-1. All values have been converted to the equivalent concentration of free carbon to allow direct comparisons. In general, the IC and GC analyses agree fairly well, but the TOC values are higher for the Shawnee samples.

The values listed in the residue column in Table 7-1 were obtained by evaporating the solvent from a portion of the acid extract. The relative agreement with the IC and GC results indicates that all of the extracted

TABLE 7-1. PRESENTATION OF ORGANIC ANALYSES BY SEVERAL TECHNIQUES

Sample Description	Date	IC ¹	Organic Carbon Concentration (mMoles C/l)			
			GC ²	TOC ³	Shawnee Analysis	Residue ⁴
Adipic Acid Std. (62 mMoles C/l)		62	61	62	--	--
Laboratory Test Filtrates						
Test 1		56	61	60	--	--
Test 2		54	54	53	--	--
Test 3		56	49	53	--	--
Test 4		57	59	61	--	--
Shawnee Pilot Samples						
Oxidizer Bleed #1	4/26/79	61	51	73	62	
Thickener Feed #1	4/26/79	58	48	75	--	
Oxidizer Bleed #2	4/26/79	54	45	75	62	
Thickener Feed #2	4/26/79	52	43	75	--	
Oxidizer Bleed #3	4/27/79	64	46	92	--	62
Thickener Feed #3	4/27/79	62	50	88	--	
Oxidizer Bleed #4	4/27/79	64	51	88	62	72
Thickener Feed #4	4/27/79	64	50	98	--	63

¹Ion Chromatography

²Gas Chromatography

³Total Organic Carbon Analysis

⁴Residue from complete evaporation of ether from acid extraction.

components are being identified and measured. The higher TOC values indicate that a portion of the organic fraction originally in the solution is not being removed during the extraction.

7.2 VARIATIONS IN EXTRACTION CONDITIONS

Additional extractions were carried out at several other pH values. The results of these extractions are shown in Table 7-2.

The first basic extraction was carried out at pH 12 after the solution had first been extracted at a pH of 1. The ether was evaporated from the basic extract and the residue was weighed. Less than an equivalent of 10 ppm adipic acid was found in this fraction. The second basic extraction was done on a fresh aliquot. No residue was observed upon the complete evaporation of the ether.

The third extraction was carried out on a sample previously extracted at pH 1. Additional acid was added to lower the pH below 0.1 and the extraction was done with ether. The extract was evaporated and 40 mg of residue was measured. An infrared analysis of the residue revealed some adipic acid but the bulk of the material was not identified. The infrared spectra of the residue and adipic acid are shown in Figures 7-1 and 7-2. The organics recovered during this extraction represent about half of the difference between the TOC value and the GC values. Further investigation of this extracted fraction appears warranted in view of the inability to close material balances around the scrubbers.

7.3 TOC ANALYSIS OF EXTRACTED FILTRATES

In addition to the investigation of the extractability of other organics as a function of pH, total organic carbon analyses of the aqueous fraction after an acid extraction were done. Blanks were run to determine whether residual ether from the extraction would interfere. It was found that the samples required vacuum evaporation to remove the ether. The results of the time study as well as the sample results are shown in Table 7-3.

Two aqueous portions after acid extractions were subjected to vacuum evaporation and then analyzed to determine the TOC value. An additional equivalent of 11 mM/l or 270 mg/l as adipic acid was measured in the aqueous fraction by the TOC analysis. This value is close to the 400 mg/l value obtained by extracting at the very low pH discussed previously.

TABLE 7-2. EFFECT OF pH ON ORGANIC EXTRACTION OF SHAWNEE SCRUBBER SAMPLES

Sample Description	TOC	GC ¹ (mmole C/l)	Extraction pH		Results
			Original	Second	
Thickener Feed #3	88	50	pH 1	pH 12	Less than 1 mg residue recovered in second extraction which represents less than 10 mg/l in the original solution.
Thickener Feed #3	88	50	pH 14	--	No residue could be detected upon evaporation of the solvent.
Oxidizer Bleed #3	92	46	pH 1	pH < 0.1	Upon evaporation of the solvent 40 mg of crystalline material was recovered. Infrared analysis revealed that the material contained adipic acid but the bulk of the residue has not been identified. This quantity represents about 40 mg/l as adipic acid in the original sample.

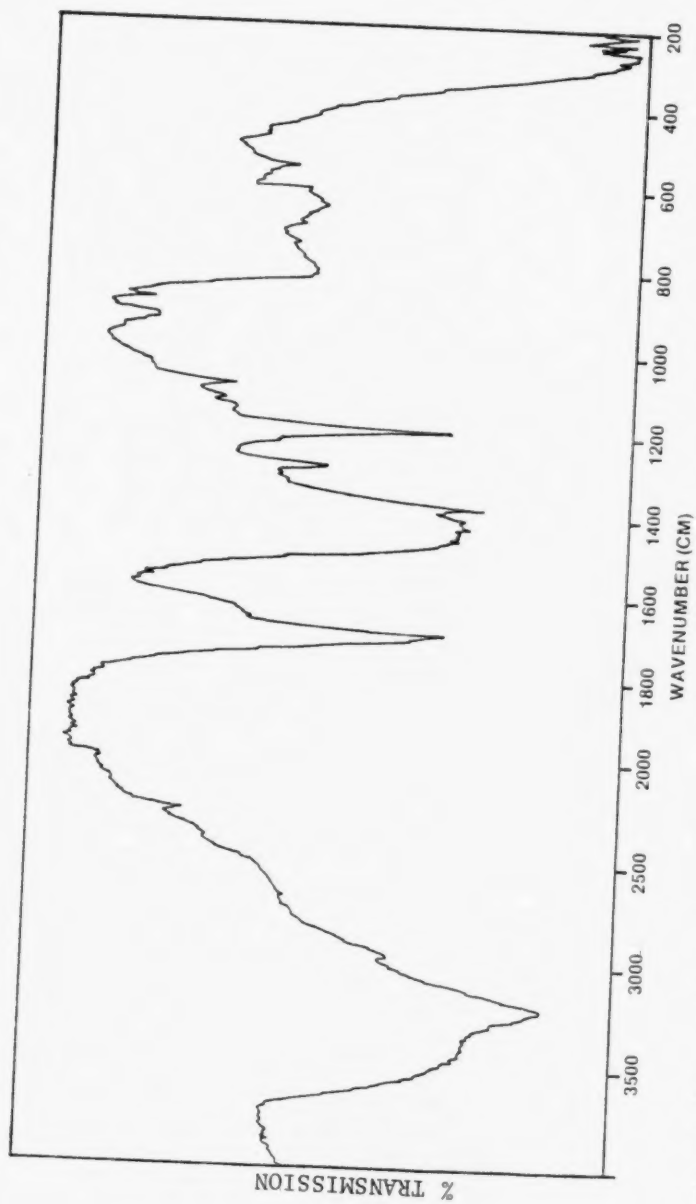


Figure 7-1. Infrared spectrum of residue from low pH extraction (Shawnee Sample #127).

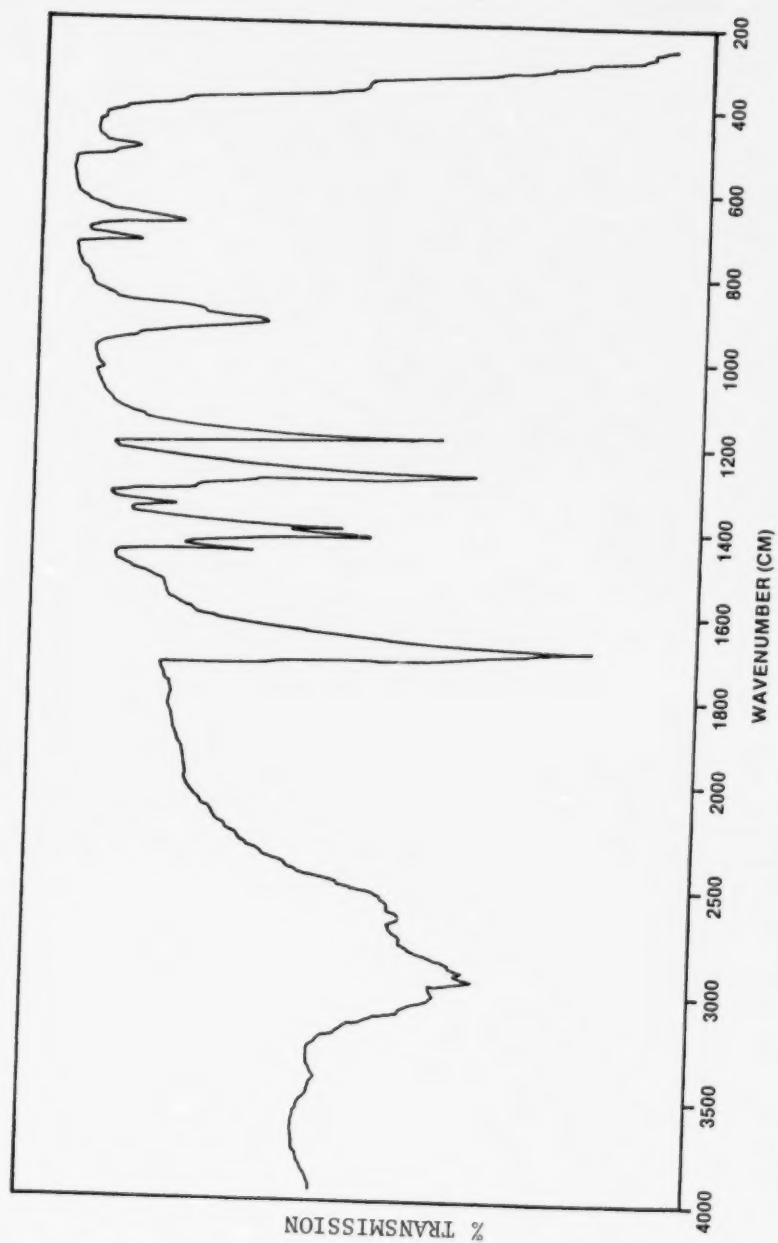


Figure 7-2. Infrared spectrum of adipic acid standard.

TABLE 7-3. TOC ANALYSIS OF EXTRACTED FILTRATES FROM SHAWNEE SAMPLES

Sample Description	Minutes Under Vacuum	GC Analysis ¹	TOC Analysis (mM Carbon/Liter as Adipic Acid)
DI Water Saturated with Diethyl Ether	5	--	0.3
DI Water Saturated with Diethyl Ether	15	--	0.3
Thickener Feed, #4	15		10.5
Thickener Feed, #4	5		11.2

¹Total organic species as determined by gas chromatography.

APPENDIX A
ANALYTICAL METHODS

1.0 ION CHROMATOGRAPHY

Ion chromatography (IC) is a relatively new technique for identifying and quantifying ions in solution, which offers the advantage of direct measurement of the concentration of the ions of interest. Ion exchange columns are used to separate the ions which are then detected through a conductivity meter. At low concentrations conductivity is directly proportional to concentration and is virtually linear. Concentrations of ions in the sample are determined by comparison with standard solutions. Identification of ionic species is based upon retention time of the ion in the system, which is a function of the affinity of that ion for the separator column under a given set of operating conditions. The retention time of specific ions is determined by analysis of standard solutions containing the species of interest.

A Dionex Model 14 ion chromatograph equipped with standard anion separator (3 x 500 mm) and suppressor columns was used for all IC work associated with this project. The eluent used for most analyses was 1.50 mM NaHCO_3 and 1.20 mM Na_2CO_3 , prepared as needed in 4 liter batches from stock solutions. In some cases column performance allowed the use of a stronger eluent while maintaining adequate peak resolution. In these cases a 2.25 mM NaHCO_3 /1.8 mM Na_2CO_3 eluent was used. Eluent flow rate was generally set at 30%. Under these conditions, adipate, chloride, sulfite and sulfate may all resolved and quantified. Statistical evaluation of data generated in the previous program indicated that the root mean square error (RMS) is approximately 7% over the range of adipate concentrations. Table A-1 details response characteristics for the species of interest under normal conditions.

TABLE A-1. RESPONSE CHARACTERISTICS OF SPECIES ANALYZED BY DIONEX

Anion	Retention Time	Relative Response	Working Range
Cl^-	~ 4 min.	15 $\mu\text{mho}/\text{mMole}$	0.005-5mM
Adipate	~14 min.	1 $\mu\text{mho}/\text{mM}$	0.01-2mM
$\text{SO}_3^{=}$	~19 min.	4.5 $\mu\text{mho}/\text{mM}$	0.03-6mM
$\text{SO}_4^{=}$	~31 min.	3.8 $\mu\text{mho}/\text{mM}$	0.03-6mM

PREPARATION OF REAGENTS AND STANDARDS

1.1 Eluent Stock Solution

Weigh out 25.2 g of NaHCO_3 and 25.4 of Na_2CO_3 and dilute to 500 ml with deionized water.

1.2 Eluent Working Solution

To prepare a 1.5 mM NaHCO_3 , 1.2 mM Na_2CO_3 eluent solution, dilute 10 mls of the stock solution to 4 liters with deionized water. The 2.25 mM NaHCO_3 , 1.80 mM Na_2CO_3 eluent is prepared by diluting 15 mls of stock solution to 4

liters.

1.3 Adipic Acid Stock Solution

It is convenient to prepare a 6000 ppm stock solution of adipic acid, and then prepare working solutions for standards and for bench test use by dilution of the stock solution. The stock is prepared by first drying ~ 7 g of adipic acid. After desiccating for several hours, weigh six grams to the nearest 0.01 mg. Transfer quantitatively to a one liter volumetric flask and add ~ 700 ml of deionized water. Mild heating and swirling may be necessary for complete dissolution of the solid. Allow the flask to cool to room temperature before diluting to the mark.

1.4 Analytical Procedure

- The ion chromatograph is initially allowed to stabilize under the analysis conditions (30% flow, with analytical eluent, etc.) until a stable base line is obtained.
- Several standards over the range of interest are analyzed and a calibration curve is obtained by plotting peak height vs concentration.
- Samples are analyzed for $2\frac{1}{2}$ to $3\frac{1}{2}$ hours.
- One or two "check" standards are analyzed to see that the machine response is not drifting, and is still functioning properly.
- Samples are again analyzed for several hours.
- Standards are again run and a calibration curve obtained at the end of the day.

2.0 SULFITE ANALYSES

$\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ solids generated for use in the bench scale degradation tests, as well as solids samples taken during the test, were analyzed to determine sulfite concentration by an iodometric titration with sodium arsenite.

In this procedure the sample is added to an excess of buffered iodine solution. The iodine remaining after the stoichiometric oxidation of sulfite is titrated with standard sodium arsenite solution. An amperometric dead-stop method was used for the endpoint detection. The analytical procedure is detailed below.

2.1 Equipment

- 50 ml buret
- Magnetic stirrer
- Pipets (10 ml); bulb pipet fillers; and 100 ml graduated cylinder
- 150 ml beakers
- 4-ounce small mouth glass bottles
- microammeter apparatus:
 - 2 1-cm square platinum-sheet electrodes mounted about 1 cm apart
 - 1.5 volt dry cell battery
 - electrometer or microammeter 0-25 μamp
 - voltage divider
- Laboratory analytical balance accurate to 0.05 mg

2.2 Reagents and Solutions

- Sodium arsenite stock solution (~ 0.010 mole/l)

Dissolve 1.3 grams of NaAsO_2 into one liter of D.I. water. Standardize this solution using reagent grade 0.1 N standard iodine.

$$(\text{molarity of NaAsO}_2) = \frac{(\text{ml I}_2) (\text{normality of I}_2)}{(\text{ml NaAsO}_2)}$$

- Preparation of a 0.1 Normal Iodine Solution

Dissolve 25 grams of potassium iodide (KI) in as little D.I. water as possible. Accurately weigh 12.69 grams of resublimed iodine and dissolve it completely in the saturated potassium iodide solution. When the dissolution of the iodine is completed, dilute with D.I. water accurately to one liter. A larger solution can be made up at one time, if desired. Iodine should be kept in a well stoppered, dark colored bottle, in a cool place. It need not be standardized if only used for the sulfite analysis since a blank is also run.

- pH 6 Buffer

This solution contains 1 mole/l NaAc and 0.05 mole/l HAc. Pipet 2.9 ml of glacial acetic acid into 500 ml of D.I. water. Stir in 82 grams of NaAc and when completely dissolved make up to one liter. It is convenient to prepare several liters of this solution at a time since 50 ml is used for each analysis.

2.3 Procedure

- Weigh 50 mg of dry solid sample to the nearest 0.1 mg.
- Pour 100 ml of pH 6 buffer solution into a 4 oz glass bottle with cap, and stirring bar.
- Pipet 10 ml of 0.1 N standard iodine solution into the bottle, cap, and begin stirring.
- Add the weighed solid sample and recap.
- Stir for 15 minutes.
- Empty bottle quantitatively into a 150 ml beaker.
- Place the platinum electrodes in the solution, stir and connect the microammeter. The current should be 30-50 microamps.
- Begin the titration with the 0.11 mole/liter sodium arsenite solution using the 50 ml buret. The color of the solution serves as a rough indicator of the state of the titration. The iodine color (red) changes to yellow 5 ml before the endpoint is reached. When the solution turns light yellow, the titration should be carried out dropwise. The solution will become colorless one to two drops before the endpoint. The titration is completed when the current reaches 3-4 microamp.
- After the titration is completed, record the volume of sodium arsenite used and rinsed the electrodes with D.I. water after removing them from the solution.
- Blanks are to be run each day using the above procedure without the addition of sample.

2.3 Calculations

The concentration (mmole/gram) of sulfite present in the solid sample can be determined by use of the following equation:

$$C = \frac{(B-S)M}{W}$$

where,

- C = concentration of sulfite (in mmoles/g)
- B = volume of arsenite used to titrate the blank, in ml
- S = Volume of arsenite used to titrate the sample in ml
- M = concentration of the sodium arsenite (moles/l)
- W = weight of sample used, in grams

3.0 INFRARED ABSORPTION SPECTROPHOTOMETRY

Calcium sulfite solids, generated to simulate scrubber solids in the bench scale tests, were analyzed by infrared spectrophotometry using a Perkin Elmer Model 283 spectrophotometer. This analysis provided a preliminary qualitative characterization of the CaSO_3 solids. A verification of the solids' sulfite concentration was later made using an iodometric titration method.

Infrared analysis was also performed on field samples collected at the Shawnee test facility and on samples collected during the laboratory testing. These samples included solids samples and filtrate extract residues.

Infrared analysis was also performed on organic residues from evaporated ether extracts of Shawnee and bench scale filtrates.

The major limitation of infrared analysis is that the technique is primarily qualitative. However, with care the relative amounts of CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ in scrubber solid samples can be determined providing limestone utilization and oxidation ratios. Detection limit for organic compounds in scrubber solids by direct IR analysis is approximately 0.1% or 1000 ppm.

4.0 CARBONATE, CARBON DIOXIDE ANALYSES

The material balance tests described in Section 6 employed sodium hydroxide impingers for trapping carbon dioxide generated in the decarboxylation of adipic acid. These NaOH solutions were analyzed for CO₂ using an Oceanography International Model 0524 non-dispersive infrared CO₂ analyzer. In this system, CO₂ is liberated after injection of the sample into an acid solution. The CO₂ is detected by the infrared analyzer and monitored by a recorder equipped with a disc chart integrator. The integrated peak area is then used to determine the amount of CO₂ present in the sample.

Samples of the NaOH solution used to trap CO₂ were preserved prior to analysis by addition of an ammonia-EDTA buffer solution to maintain a pH of ~10. Samples of this buffer solution and of the stock NaOH solution were analyzed to determine background levels of CO₂ present in these solutions. These blank values were taken into account in the calculation of the amount of CO₂ generated in the degradation reaction.

This method of CO₂ determination is quite specific, especially when the sample matrix is well defined as in this application. The analyzing unit allows samples to be analyzed without introducing atmospheric carbon dioxide. Water vapor is removed from the gas stream by a series of drying tubes upstream of the detector. By using peak area instead of peak height, inaccuracies due to varying pH in the acid pool are virtually eliminated. Analytical Procedures are outlined below.

4.1 Reagents and Solutions

4.1.1 Sodium Carbonate Standard Solution

A 100 ppm CO₂ standard solution is prepared by accurately weighing 0.2410 g of dried, desiccated Na₂CO₃ and volumetrically diluting to one liter with boiled, cooled deionized water.

4.1.2 Acid Solution

In preparing the acid solution it is convenient to first prepare stock solutions of 5% H₃PO₄ and 10% KH₂PO₄. The 5% H₃PO₄ solution is prepared by diluting 5 ml of concentrated H₃PO₄ to 100 ml with deionized water. The 10% KH₂PO₄ solution is prepared by dissolving 100 g KH₂PO₄ in 900 ml of deionized water.

Using the stock solutions, the working acid solution is prepared by mixing 95 ml of 10% KH₂PO₄, 5 ml of 5% H₃PO₄ and 1 ml of 30% H₂O₂. To this solution is added several drops of methyl red indicator.

4.1.3 Buffer Solution

The ammonia-EDTA buffer solution used for preservation of the CO₂

samples is prepared in the following manner. Measure out 142.5 ml of fresh (or nitrogen or argon blanketed) NH_4OH (concentrated reagent) in a 250 ml graduated cylinder. Weigh out 17.5 g NH_4Cl and dissolve in less than 100 ml of deionized water, then add to NH_4OH and dilute to 250 ml. Weigh out 200 g of $\text{Na}_2\text{-EDTA}$ and dissolve in the $\text{NH}_4\text{OH-NH}_4\text{Cl}$ solution. Store buffer solution in a full, tightly sealed bottle.

4.2 Procedure

- Turn power on and allow instrument to warm-up over night.
- Turn nitrogen on and make flow adjustments.
- Inject 2-3 ml of acid solution into sample chamber.
- After 2 or 3 minutes purge, set instrument zero.
- Inject 200 μl of the 100 ppm CO_2 standard and set instrument span so that the resulting peak is ~65% of full scale on the chart recorder.
- Proceed with injection of standards, 200, 150, 100 and 50 μl injections are recommended, with triplicate injections for each volume.
- Change acid pool as indicated by a change in color from red to yellow-orange.
- Proceed with analysis of samples, including injections of the buffer solution for blank determination.
- Standards should be run at the beginning and end of the analysis, with additional standards during the analysis if the duration exceeds three hours.

4.3 Calculations

A calibration curve is derived from the standards data by fitting the points to a linear equation of the form $y = ax + b$, where:

- y = wt. of CO_2 (μg)
- a = slope
- x = peak area
- b = y intercept

following calculation of regression coefficients (a and b), corresponding values of y can be found for given values of x .

The concentration of CO_2 in the original sample is calculated from the formula

$$S = \frac{B(G/p + F) - C_fVF}{(G/p) VM}$$

where,

- S = Concentration of CO₂ in original sample (moles CO₂/liter)
- B = Total weight of CO₂ in volume V (μg) (from calibration curve)
- G = Weight of aqueous sample
- P = Density of sample (g/ml) (use 1.00 unless density is measured)
- F = Volume of buffer solution added to sample (ml)
- C_f = Concentration of CO₂ in fixing solution (μg/μl)
- V = Actual volume of sample aliquot injected (μl) and
- M = Molecular weight of CO₂ (44.0099 grams/mole)

5.0 TOTAL ORGANIC CARBON ANALYSES

Total Organic Carbon (TOC) analyses were performed on samples collected at Shawnee and on samples generated in the laboratory material balance tests. All TOC determinations were made using an Oceanography International non-dispersive infrared CO₂ analyzer. The procedure used is basically a modification of the procedure outlined for carbon dioxide analyses. In the TOC procedure, inorganic carbonate present in the sample is first liberated as CO₂ by acidification of the sample followed by an oxygen purge. The sample is then sealed in a glass ampule in the presence of potassium persulfate. The sealed ampules are heated to ~550°C for four hours, quantitatively oxidizing all organic carbon to CO₂. The CO₂ is ultimately flushed out of the ampules and into the analyzer with a N₂ purge as described in the section on CO₂ analyses. Potassium hydrogen phthalate standards are prepared and analyzed in the same manner as the samples. A standard curve is obtained by plotting concentration vs peak area, as before.

6.0 DETECTION OF LOW MOLECULAR WEIGHT HYDROCARBONS

6.1 Collection

Low molecular weight hydrocarbons were removed from the Shawnee oxidizer vent gas stream and from the laboratory bench test exit stream using activated carbon and silica gel traps. The traps consisted of 3/8" O.D. x 24" long stainless steel U-tubes packed with 30 ml of either activated carbon or silica gel.

A measured volume of the gas stream of interest was passed through the tube at 15-30 ml per minute at 0°C. After passage of the calculated gas volume, the U-tube was sealed.

6.2 Desorption and Analysis

The trap was desorbed in a 200°C oven. Dry nitrogen was passed through the trap into a 2 liter evacuated gas bomb at 50 mls per minute until the bomb reached atmospheric pressure.

The contents of the bomb were analyzed on a Hewlett-Packard HP 5730A temperature programmable gas chromatograph with an HP 3380 integrator. Conditions for analysis are listed below.

Column: 6' x 1/8" i.d. stainless steel, packed with Chromo-sorb 102, 80/100 mesh

Carrier Gas Flow: N₂, 30 ml/min

Temperature Program: 135°C initial temperature
16°C per minute
200°C final temperature

Detector: Flame ionization

Traps are repeatedly purged until GC analysis indicates blank levels of hydrocarbons.

8.0 PREPARATION OF SOLIDS FOR ORGANIC ACID ANALYSIS

0.2g of solids dried at 50-60°C is weighed on an analytical balance and placed in a graduated 150 ml beaker. 100 mls of 2N H₂SO₄ is added and the solution is stirred for 30 minutes to 1 hour. The solution is transferred quantitatively including any undissolved solids to a 1000 ml separatory funnel. The solution, is extracted, concentrated, derivatized with Diazomethane, and stored in the same manner as the NaOH impinger extracts described in Section 7.0 in this appendix.

7.0 EXTRACTION OF LIQUIDS FOR ORGANIC CARBON

Scrubber filtrates, laboratory test filtrates, and NaOH impingers are extracted for organic acids using the following method:

100 mls of solution is pH'ed to 1.9 using concentrated HCl and a pH meter. It is transferred quantitatively into a 1000 ml separatory funnel and extracted with five 150 ml aliquots of diethyl ether. The ether extracts are combined and dried over anhydrous sodium sulfate. After drying, the solution is decanted quantitatively into a 1000 ml Kaderna-Danish apparatus with 20 ml receiver. A boiling chip is added and a macro distillation column placed on top. The ether extract is concentrated over a steam bath to about 50 mls if it is a filtrate and to about 5 mls if it is an impinger.

Filtrate extracts are transferred quantitatively to 100 ml volumetric flasks and made up to volume. A pasteur pipet is used to transfer about 1 ml of solution to a 1 ml hypovial and the liquid level marked. A 1% solution of Diazomethane in diethyl ether is added until the yellow color remains. The solution is allowed to decolorize and evaporate to the liquid level mark. It is sealed with a septum and septum cap and stored at 10°C.

NaOH extracts are further concentrated to 1 ml in a 20 ml receiver with micro distillation column. The solution is transferred to a 1 ml hypovial and handled in the same way as the filtrates described above.

Extraction cannot be expected to remove all adipic acid present. Extraction of standards has yielded the following extraction efficiencies to which all gas chromatographic analyses are corrected:

Adipic Acid	87% + 7% (4 standards)
Valeric Acid	82% (1 standard)
Glutaric Acid	87% (assumed to be the same as adipic acid)
Succinic Acid	87% (assumed to be the same as adipic acid)

9.0 GC ANALYSIS OF ETHER EXTRACTS

Samples were analyzed for adipic, valeric, glutaric, succinic, and butyric acids on a Hewlett-Packard Model 5730A gas chromatograph with a dual flame ionization detector. Peak areas were integrated with a Hewlett-Packard Model 3380A integrator. Conditions for analysis are listed below:

Column: 9 ft x 2 mm ID glass, packed with 10% SP-2340 on Supelcoport,
80/100 mesh
Carrier Gas, Flow: N , 30 mls/min
Oven Program: Initial - 50°C, 4 minutes
Rate - 32°C /minute
Final - 150°C, hold 4 minutes

APPENDIX B

LABORATORY GENERATION OF $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ SOLIDS

In the bench scale degradation tests, scrubber solids were simulated with $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ solids. These solids were prepared by titrating a 0.77 M CaCl_2 solution with a 0.77 M solution of Na_2SO_3 . By titrating the CaCl_2 solution with the Na_2SO_3 , vacuum filtering the precipitated $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ and oven drying at 50°C , approximately 80% pure solids could be produced. The primary impurity was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ formed by oxidation during preparation.

Modifications of the basic procedure made it possible to consistently prepare solids of greater than 95% purity, and as high as 99+% in some cases. The major points in the modified procedure are:

- The deionized water used to prepare the CaCl_2 and Na_2SO_3 solutions should be boiled and cooled while purging with N_2 . This assures that a minimum amount of dissolved oxygen is present.
- All steps in the solids preparation including solution preparation, titration and filtration should be carried out in a nitrogen atmosphere.
- After filtration, the prepared solids should be washed by re-slurrying in the O_2 free water and re-filtering. Any $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ which has formed will be preferentially dissolved in this step.
- Following the second filtration the solids should be washed with N_2 purged acetone to eliminate the bulk of the entrained moisture before oven drying at 50°C .

APPENDIX C
GAS CHROMATOGRAMS OF SOLIDS ANALYSIS

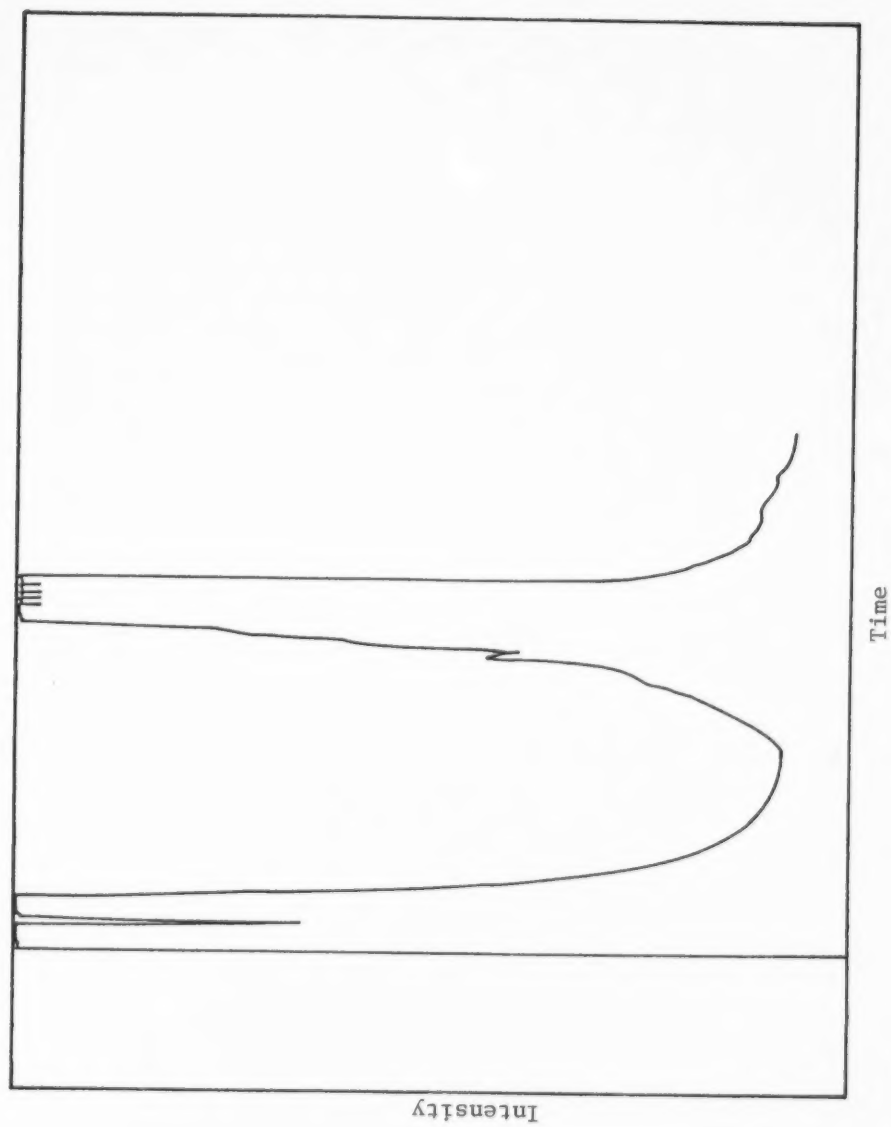


Figure C-1. Sample GC chromatogram of solids blank.

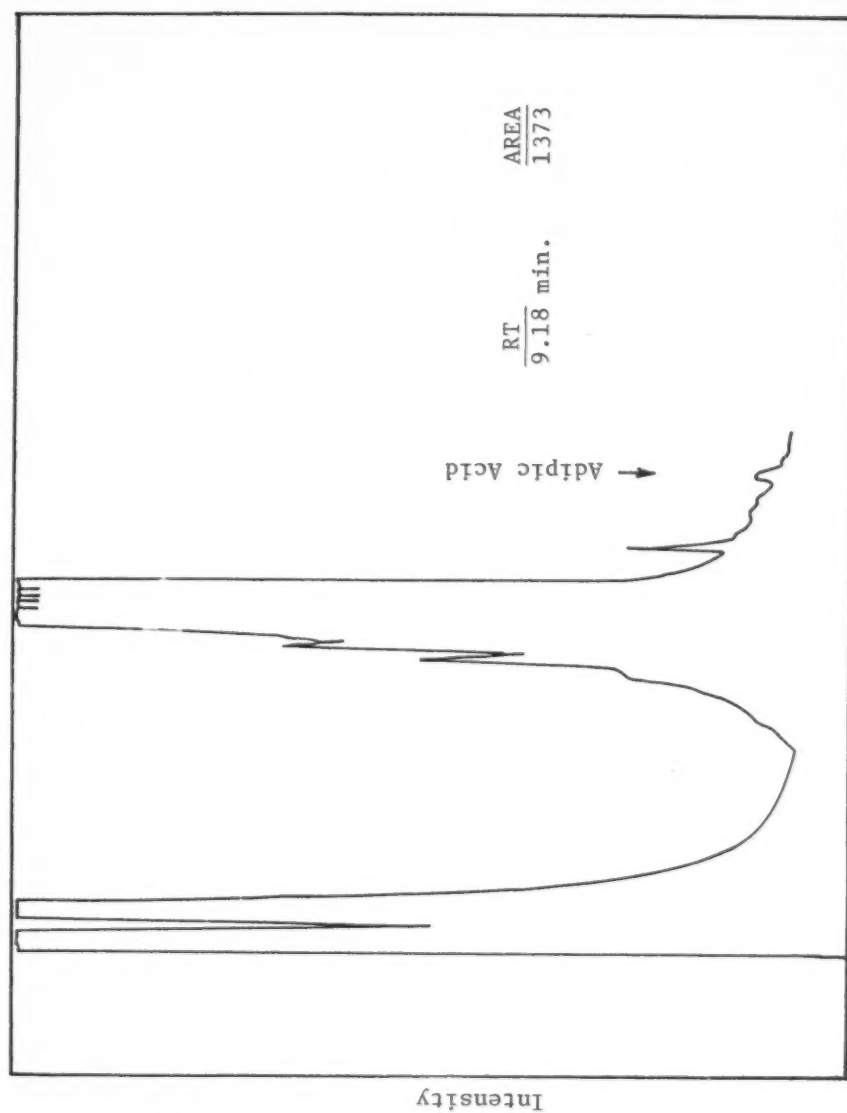


Figure C-2. Sample GC chromatogram of solids sample.